Post-Irradiation Polymerization of a Silorane Composite

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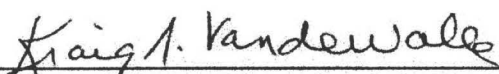MASTER OF SCIENCE

In Oral Biology

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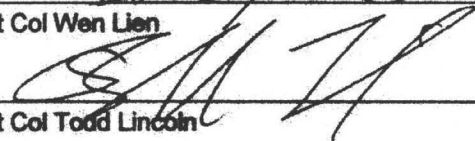
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26 Apr 2013

Post-Irradiation Polymerization of a Silorane Composite Resin

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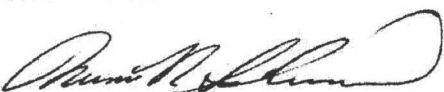_Kraig A. Vandewalle_
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ABSTRACT

Objective: To characterize the post-irradiation conversion of a silorane composite. Specifically, to determine the time and amount of conversion that occurs for the selected silorane composite, and to compare these parameters with those established in the literature for methacrylate based composites. **Methods**: Silorane composite (Filtek LS) samples of 0.5 mm thickness were placed on the attenuated total reflectance (ATR) attachment of a Fourier Transform Infrared Spectroscopy (FTIR) device. Spectra were measured immediately after photo curing and at specified post-irradiation times up to 10 days. **Results:** The silorane achieved 65% of its observed maximum degree of conversion (DC) immediately after photoinitiation, 80% in 1 hour, 90% in 1 day, 95% in 5 days, and 99% in just over 8 days of the 10-day observation period. DC increased by 53% in the post-irradiation phase, corresponding to 28 percentage points, accounting for 35% of total conversion. Observed 24-hour conversion +/- standard deviation was 71 (+/-5)%. Measured maximum post-cure conversion during the 10-day testing period +/- one standard deviation ranged from 72-85%. **Conclusions:** The post-irradiation conversion of a silorane composite, Filtek LS, follows a pattern and rate (curve shape) similar to methacrylate composites. The proportion of conversion as measured by DC accounted for by post-irradiation conversion is slightly higher than that reported for methacrylates (as measured by hardness), and the duration of post-irradiation conversion is longer. Final degree of conversion is similar to that reported for methacrylates.

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I.   BACKGROUND AND LITERATURE REVIEW

A. Factors Affecting Methacrylate and Silorane Composites

Composites based on a silorane-resin system have recently become commercially available and are the only alternatives to the methacrylate resin-based composites that have been in use since the beginning of dental composites. Siloranes were introduced as a new dental material, which due to their different, ring-opening polymerization chemistry of the resin component, have a significantly decreased polymerization shrinkage compared to traditional methacrylate resins (Guggenberger and Weinmann, 2000). Subsequently, their development by 3M-ESPE (Weinmann et al, 2005) has led to the current commercial system. The new silorane-based composites exhibit approximately 1% shrinkage compared to 1.5-5% that is typical of traditional methacrylates (Duarte et al, 2009; Ferracane, 2005). Silorane composites have chemical and mechanical properties comparable to traditional methacrylate composites, with some improved properties including decreased leachability, better dimensional stability, and greater hydrophobicity (Lien and Vandewalle, 2010; Ilie & Hickel 2006). Siloranes are inherently hydrophobic. They are a combination of siloxane and oxirane chemical moieties on each monomeric unit, where the siloxane provides a hydrophobic and chemically stable backbone, and the oxirane provides reactive groups that allow polymerization. The distinctive characteristic of siloranes is the ring-opening polymerization reaction of the oxirane moeity, which inherently leads to less polymerization shrinkage than the

well-known polymerization reaction of methacrylates. The first commercially available silorane composite became available in 2007, Filtek LS (3M ESPE, St. Paul, MN, USA). To maintain compatibility with the widely used LED curing lights, camphorquinone was retained as the photoinitiator. Camphorquinone is useful in methacrylate chemistry because it generates reactive free radicals. However, silorane requires a reactive, positively charged, cationic initiator. For this reason, an iodonium salt, paired with an electron donor, is used to convert the energy from the activated camphorquinone into a reactive cation initiator. The free radical-promoted cationic photo-polymerization corresponds to the excitation of camphoroquinone to generate free radicals which are oxidized by an iodontium salt, producing cations suitable for the opening of the cationic monomer ring. This 3-component initiation system, along with siloxane monomers, comprise an integrated, photopolymerizeable system to which fillers are added to form the silorane-based composite system. Filtek LS incorporates silica and radiopaque yttrium fluoride filler particles, making the incorporation of filler into the resin matrix similar to modern techniques being used for current methacrylate composites. The particles are coated with a silane layer to allow chemical bonding of the filler particles to the organic matrix. The silane layer is uniquely modified with an epoxy functionality to allow chemical bonding to the silorane resin (Weinmann et al, 2005).

The Filtek LS product suite includes a specially formulated methacrylate-based two-step self-etching adhesive system that is necessary to bond the silorane to tooth

structure. The dentin bond strength of the Filtek LS system is equivalent to that of methacrylate-based systems if the Filtek LS primer and adhesive are used. However, siloranes are not compatible with adhesives that are formulated for methacrylate composites. (Boushell et al, 2011).

To date, a limited number of studies have characterized the physical properties and polymerization characteristics of silorane dental composites. In general, Siloranes have demonstrated decreased shrinkage (Tantbirojn et al., 2011; Arrais et al., 2013), cuspal deformation and contraction stress (Palin et al., 2005; Tantbirojn et al., 2011; Boaro et al., 2010), comparable physical properties (Ilie and Hickel, 2009; Leprince 2010; Lien and Vandewalle, 2010), variable marginal leakage (Tantbirojn et al., 2011; Yamazaki et al., 2006; Krifka et al., 2012; Palin et al., 2005 and 2009; Ernst et al., 2008; Bagi et al., 2009), increased hydrophobicity (Guggenberger and Weinmann, 2000), low toxicity (Schweik et al., 2002; Schweikl et al., 2004; Kostoryz et al., 2007), stability in oral fluids (Ilie and Hickel, 2009; Brackett et al., 2007; Yesilyurt et al., 2009), and similar photopolymerization efficiency (Leprince et al., 2010; Eick et al., 2006) compared to methacrylate composites. An experimental silorane composite was found to have a significant decrease in microleakage and cuspal deflection compared to Filtek Z250 (Palin et al, 2005). In that study, the authors developed a method to evaluate the degree of conversion (DC) of siloranes with infrared spectroscopy. Notably, they found that the extent of DC was similar to that for methacrylates.

Since siloranes are a much newer material than methacrylates, the great wealth of research concerning dental composites is based on methacrylates. The physical properties of methacrylate composites are affected by both resin and filler composition and loading, which are related to polymerization stress (Sakaguchi et al, 1992). Flexural strength, flexural modulus, Vickers hardness, and fracture toughness of composites are affected by filler particle morphology and loading (Kim et al, 2002). Filler composition and loading also affect depth of cure (Eliades et al, 1987). Differences in filler content affect compressive strengths, moduli of elasticity, water sorption, and linear coefficient of thermal expansion of composites (Raptis et al, 1979). There is a positive relationship between volume fraction of filler, diametral tensile strength, and KHN number. Furthermore, the filler concentration and the nature of bonding between filler particle and resinous matrix play a prominent role in determining the properties of composites (Chung, 1990).

The physical properties of composites are dependent on the DC achieved. In particular, achieving adequate depth of cure is important in obtaining physical properties that provide clinically adequate physical and chemical stability throughout the entire bulk of a composite restoration. For methacrylate-based composites, depth of cure is one of the variables affecting clinical performance and is easily controllable by clinician technique. Methacrylate-based resin composites exhibit lower strength and greater wear if they are not optimally polymerized (Ferracane, 1985). There is a good correlation between decreasing DC and decreasing abrasive

wear resistance and hardness (Ferracane et al, 1997). There is also a good correlation between decreasing DC and decreasing fracture toughness (Ferracane and Berge, 1995). There is a strong correlation and linear relationship between hardness and DC established for methacrylate based composites (Vandewalle et al, 2004). Diametral tensile strength, hardness, compressive strength, flexural strength and modulus, and dynamic mechanical properties have been correlated with DC using Fourier Transform Infrared Spectroscopy (FTIR): there was a significant positive correlation between improved properties and increased DC (Ferracane and Greener, 1986). In contrast, decreased DC may be beneficial and lead to decreased polymerization shrinkage contraction stress (Silikas et al, 1986).

DC also affects the marginal integrity of composite resins. DC has been shown to affect the amount of remaining methacrylate groups of Bis-GMA resins (Ryuter and Svendsen, 1978). The increased availability of methacrylate monomers for leaching with decreased DC has been shown (Rueggeberg and Craig,1989). There is a significant loss in marginal integrity at gingival margins with the lowest DC after thermal-mechanical stressing of methacrylate-based composites (Vandewalle et al, 2004). This is also true for composites stored only in water, indicating that the DC has more of an effect on marginal integrity than thermo-mechanical cycling, due to the greater availability of residual monomers for leaching (Vandewalle et al, 2004). Light curing techniques may produce adequate marginal integrity even though

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properties at the bottom of restorations may be significantly less than the properties on the surface (Ferracane and Greener, 1986).

The DC of dental composite was shown to be affected by resin composition (Ryuter and Svendsen, 1978). For example lower diluent concentration and higher inhibitor concentrations significantly reduce DC (Ferracane and Greener, 1986). For a given composition of monomer, the hardness varies with content of inhibitor and peroxide, but is unaffected by changes in the content of amine (Asmussen (1982a). Monomer content of peroxide predominantly determine tensile strength, which correlated with the quantity of the remaining double bonds. Quantity of remaining double bonds correlates well with Hardness. Resin chemistry affects also affects modulus of elasticity and water sorption (Raptis et al, 1979).

Energy applied during photoinitiation also affects physical properties. DC and polymerization stress, but not the rate of polymerization, increase with increasing irradiant energy (Calheiros et al, 2008). There is a consistent cure profile as a function of total energy applied for different composites with differing resin chemistry (Halvorson et al, 2000). Knoop Hardness (KHN) decreases with depth and is affected exposure time (Cook, 1990).

Photoinitiation has been shown to produce similar levels of conversion in siloranes compared to methacrylate composites. The photoinitiation efficiency and effects of DC on physical properties are also similar between methacrylate and silorane composites (D'Alpino et al, 2011; Ilie and Hickel, 2006; Leprince et al, 2010). The silorane composite Filtek LS is an efficient photocurable material capable of acceptable (80%) bottom-to-maximum KHN ratios after 20 seconds of light exposure (Stefan-Dogar and Vandewalle, 2010).

B. Post-Irradiation Polymerization

An important factor affecting final DC of methacrylate based composites is post-irradiation polymerization. After photoinitiation ends, polymerization continues. Thus, the final DC cannot be achieved until post-irradiation conversion is completed. This issue is important in research comparing composites, the effectiveness of light curing units and photocuring regimes. It has been established that methacrylate polymerization finishes within 24 hours following photoinitiation (Leung et al, 1983; Ferracane, 1985; Pilo et al, 1992). One of the factors affecting post-irradiation polymerization is temperature. Changes in temperature are 12.5 times more important than duration of heat exposure (Bagis et al, 1997). Post-irradiation conversion is also affected by monomer chemistry. An increase in TEGDMA has been shown to result in less post-irradiation polymerization of bis-GMA-based composites (Tarumi et al, 1999). Post-irradiation polymerization is not affected by

total applied energy.   Depending on the material, post-irradiation polymerization accounts for as much as 19-26% of the final conversion of methacrylates (Halvorson et al, 2001).

II.   OBJECTIVES

The post-irradiation conversion of silorane composites has not to date been evaluated. In fact, silorane polymerization chemistry differs completely from that of methacrylate polymerization chemistry, meaning that post-irradiation polymerization may be significantly different in extent, rate, and duration. Thus, the objective of this experiment was to characterize the post-irradiation conversion of a silorane composite (Filtek LS).

III. MATERIALS AND METHODS

A.   Experimental Design Overview

Silorane-based composite (Filtek LS) was applied to the attenuated total reflectance (ATR) element of an FTIR (Spotlight 400 FTIR Imaging System, PerkinElmer, Bacon, UK), and photo-cured in place for 20 seconds. The post-irradiation FTIR spectra were obtained at various post-irradiation times. Since by nature the ATR measured the bottom sample surface, samples were made as thin as possible to simulate a top surface.

B.   Experimental Design

Filtek LS, shade A2, was expressed into a 0.5 mm-thick steel mold on the sample platform of the FTIR-ATR at the center of the specimen surface (Figure 1). Three Filtek LS samples, each from different compules but the same lot, were tested (n=3). The sample of uncured composite was covered with a Mylar strip, flattened and compressed with a torque vice. The vice was removed, and a light-emitting diode light-curing unit (LCU) (Elipar S10, 3M ESPE) was positioned with a clamp so that it was in contact with the top surface of the composite. Samples were irradiated for the manufacturer-recommended time of 20 seconds (Figure 2), the torque vice was removed, and 50 N-cm torque applied. LCU irradiance was measured with a spectrophotometer (Resin Calibrator, BlueLight Analytics, Halifax, Nova Scotia, Canada) to ensure 1200 mW/cm^2 was maintained throughout the experiment.

Samples remained on the ATR platform of the FTIR at room temperature and humidity in a light corrected room which removed other potential curing light sources for the duration of testing. To measure post-irradiation DC, spectra were obtained at the following times: immediately after photoinitiation (scanning occurred for 2 minutes following discontinuation of photoinitiation), 10 min, 20 min, 30 min, 1 hour, 2 hours, 4 hours, 8 hours, 24 hours (1 day), and every 24 hours for elapsed time of 10 days.

Figure 1: FTIR-ATR specimen surface and sample placement.
a. ATR surface

b. Sample placed on the ATR element. The center dark area is the ATR crystal.
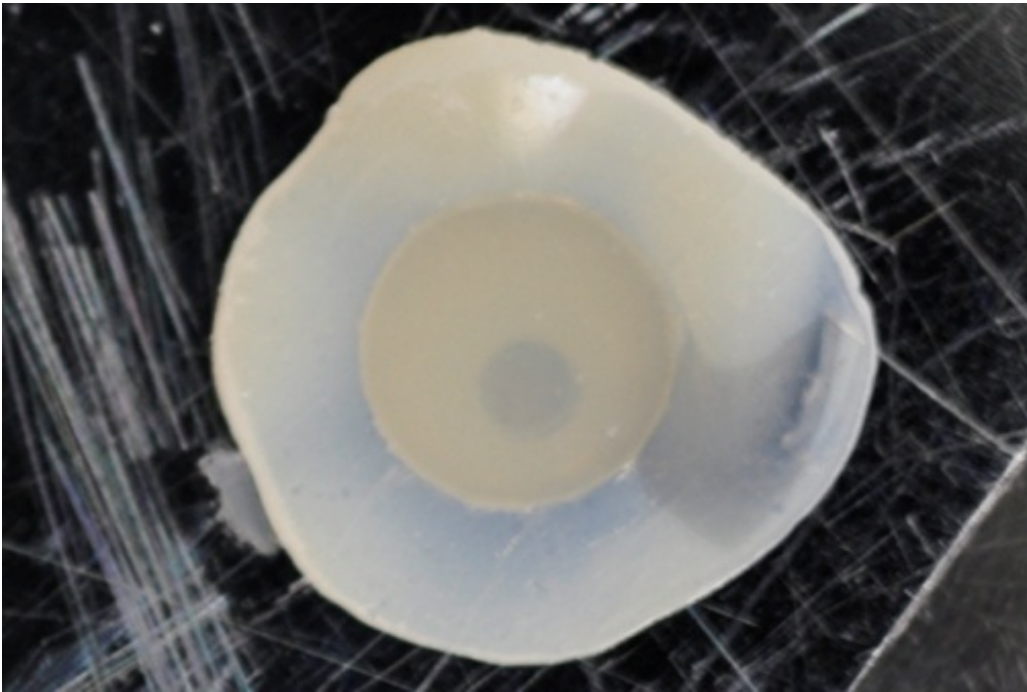
c. Transilluminated sample showing imprint of ATR crystal.

Figure 2: LCU positioning and stabilization over the sample.
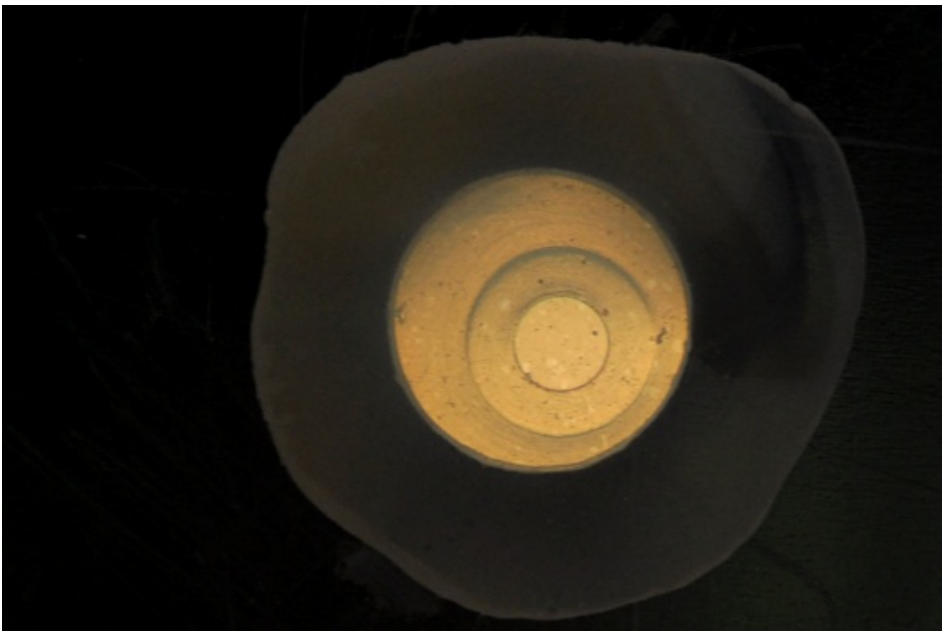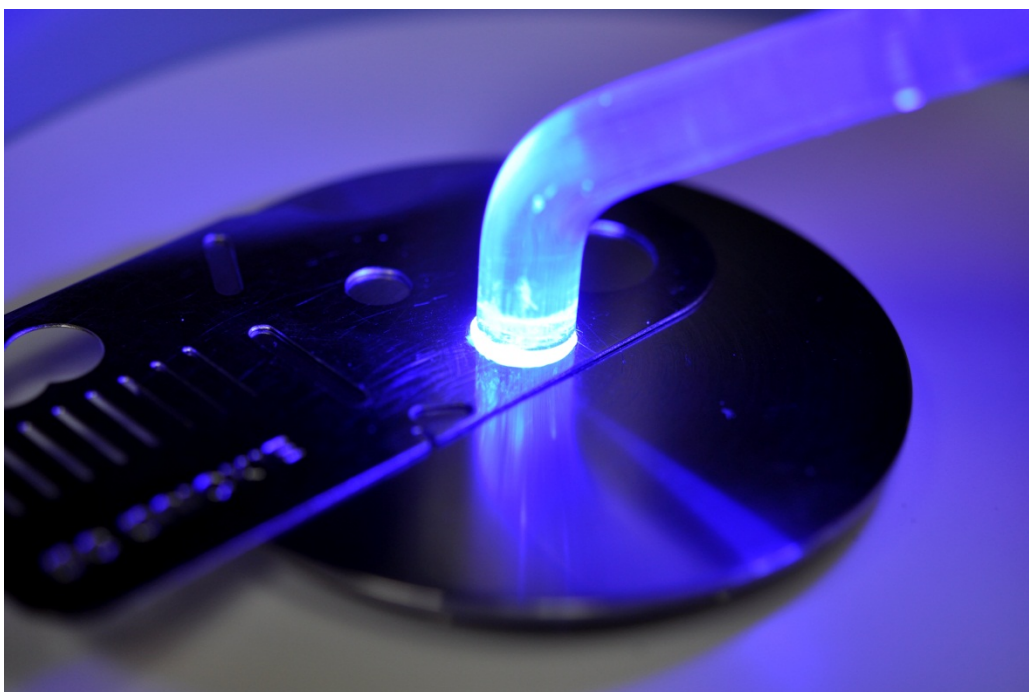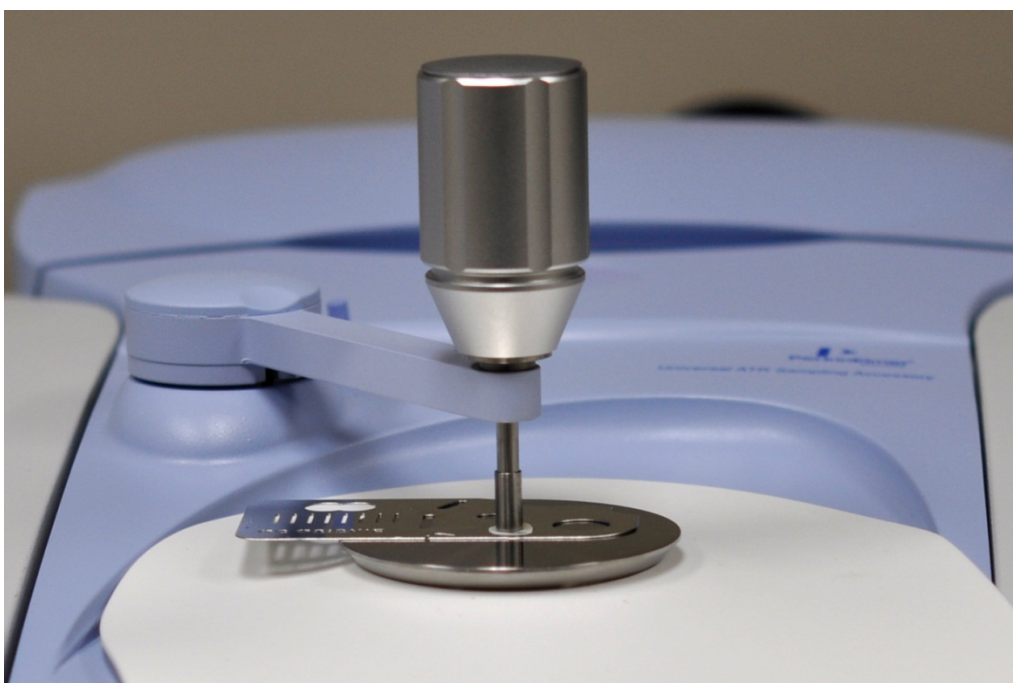
a. Stabilization of LCU over sample.

b. Photoinitiation of sample over ATR element.

c. Positioning of torque wrench over sample for 1) preparation of sample, and 2) post-irradiation sample stabilization.

To determine DC, spectra were taken under the following conditions: $4000 - 600$ cm^{-1} wave numbers range and 16 scans per spectrum at a 4 cm^{-1} spectral resolution. The DC calculation was completed through the regions of the FTIR spectra between 650 and 950 cm^{-1} which corresponded with the oxirane ring-opening regions. With silorane monomers, the stretching vibrations for the epoxy ring, C-O-C (884 cm^{-1}) and Si-CH$_3$ bonds (695 cm^{-1}) were chosen as the analytical and internal-reference absorption bands respectively (Figure 3). The DC was calculated from the ratio of the peak heights of the analytical and reference absorption bands normalized by the ratio of the uncured monomers:

$$DC\% = 100 \left[1 - \frac{\left(\frac{A_{ana}}{A_{ref}}\right)_{polymer}}{\left(\frac{A_{ana}}{A_{ref}}\right)_{monomers}} \right]$$

The A$_{ana}$ and A$_{ref}$ represent the absorbance intensities of the C-O-C (884 cm^{-1}) and Si-CH$_3$ (695 cm^{-1}) bonds respectively. DC of uncured composite was measured the same way, and an average of multiple uncured spectra was used for all calculations.

Figure 3. Silorane FTIR spectrum: 10 days of spectra superimposed.

a. Silorane spectra superimposed over 10 days of post-irradiation.
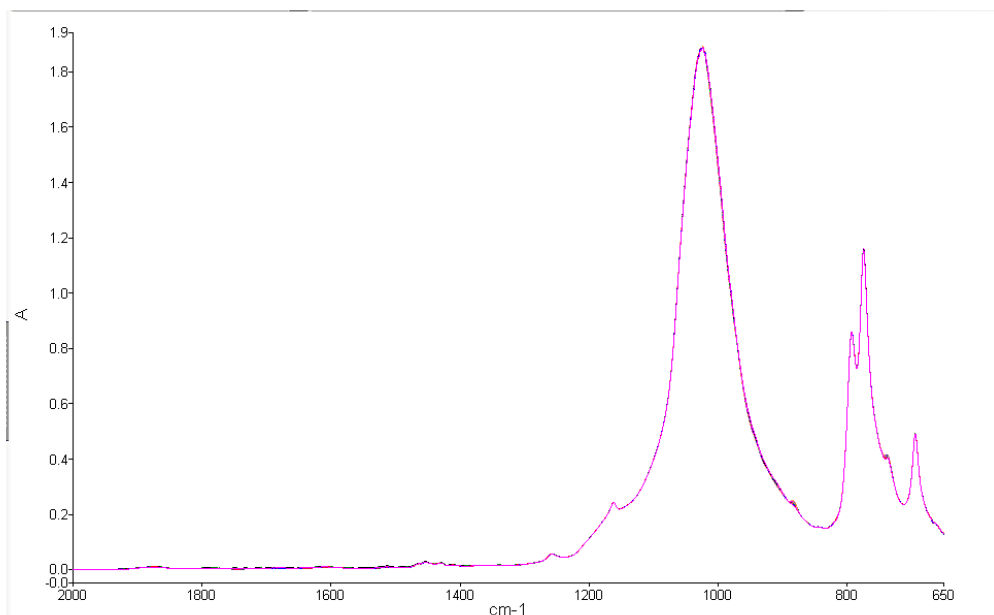
b. Analytical and internal reference bands of silorane composite: 10 days of samples superimposed. Changes to analytical band apparent.

C-O-C (884 cm^{-1}) analytical band.

Si-CH3 bonds (695 cm-1) internal reference band.
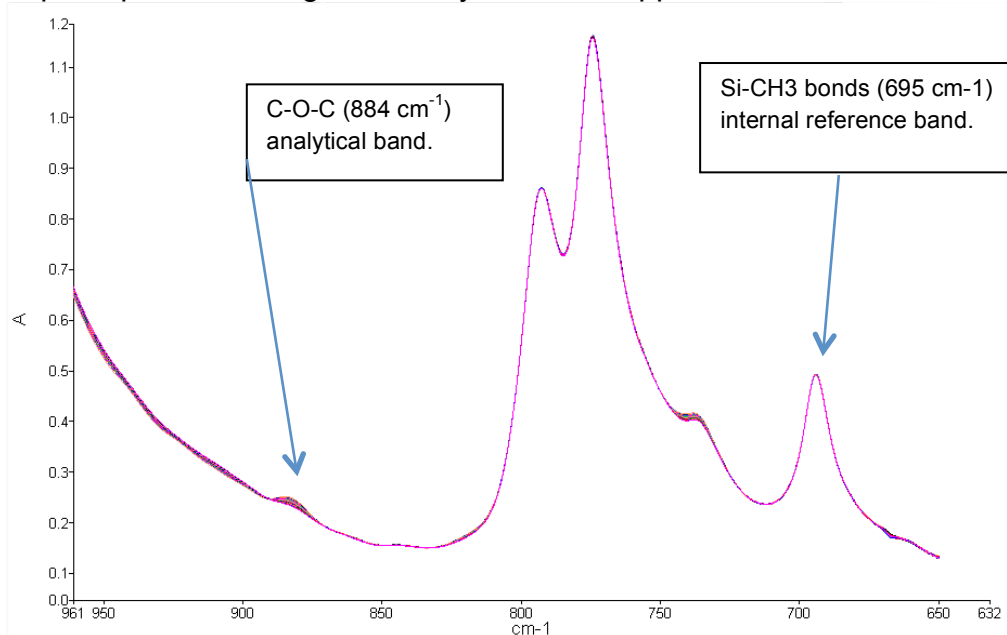
c. Analytical band of silorane composite: 10 days of samples superimposed. Changes to analytical band apparent.
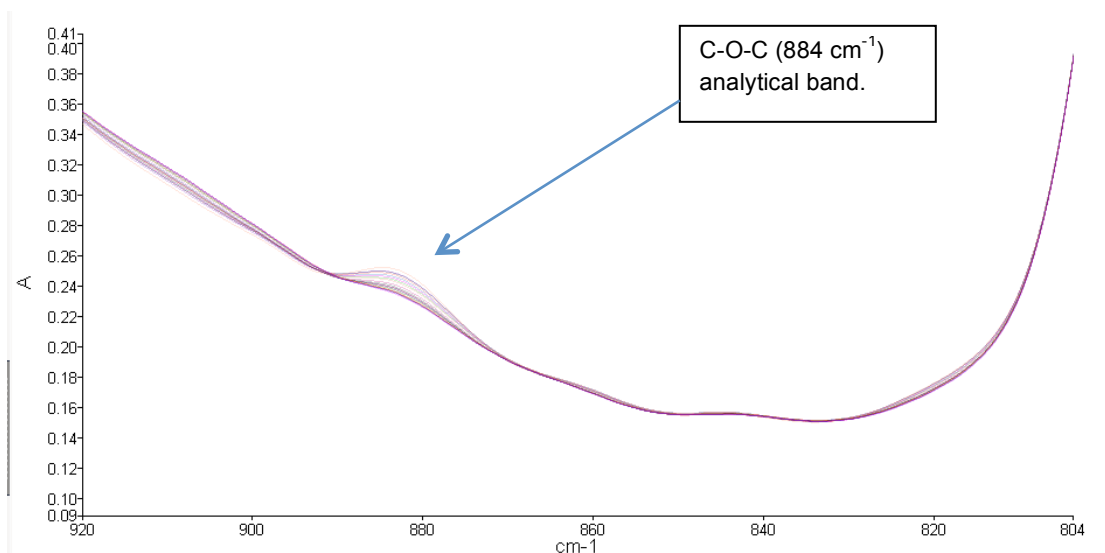
C. Measurement of Peak Heights.

Figure 4 shows how baseline and peak height were established for the analytical and reference bands. For the analytical band, the lowest inflection points on either side of the peak were chosen to establish the baseline; the height of the peak was measured by visual estimation. For the reference band, the left base of the curve was chosen as the left baseline reference; however, it was more difficult to identify an inflection point for the right side to select as the right reference for the baseline. The first slight inflection away from the main peak was selected as shown. The peak height selected by the computer was used for the reference peak.

Figure 4: Baseline and peak heights selection for analytical and reference peaks.

a. Peak height and baseline of analytical peak.
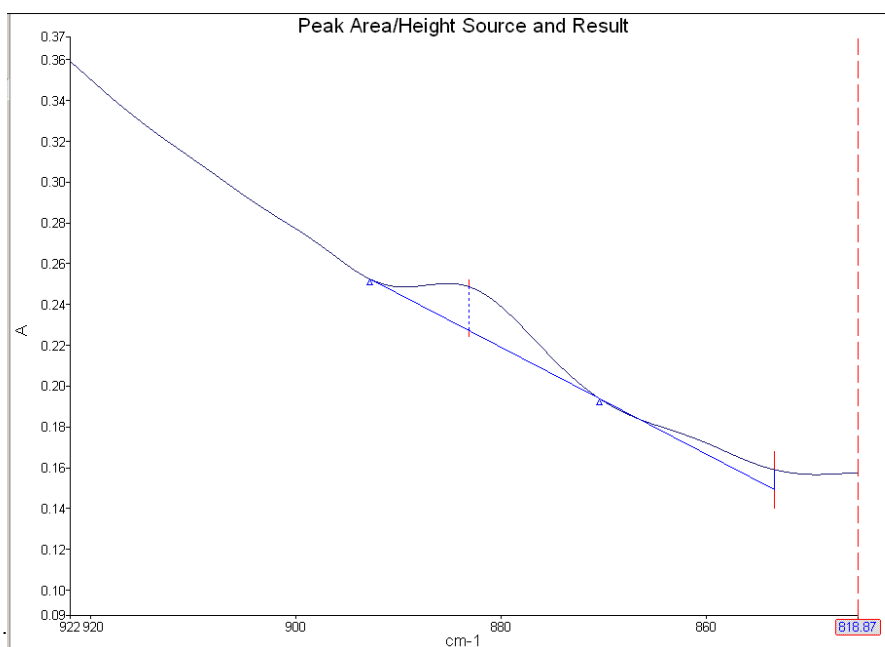
b. Peak and baseline of baseline peak
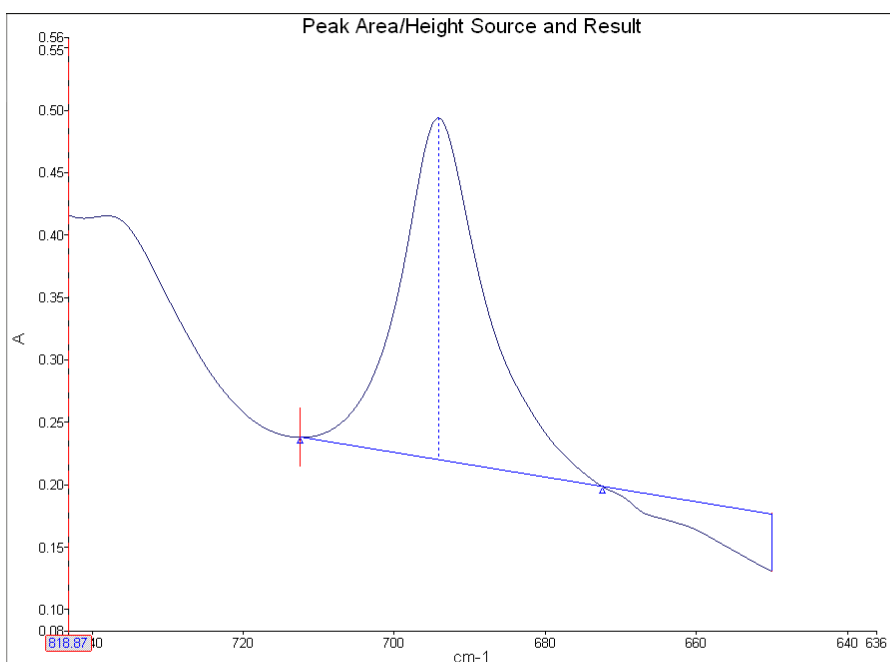
The composition of the study material, Filtek LS, is described in table 1.

Table 1. Study Materials

Composite	Type	Manufacturer	Resin	Filler	Weight %	Volume %	Filler Size
Filtek-LS	Silorane (S)	3M/ESPE, St. Paul, MN, USA	Silorane	Quartz, Yttrium Fluoride	76%	55%	0.04 - 1.7 μm

After testing, samples were removed and their thickness measured with a Boley gauge to ensure a thickness between 0.5 to 0.6mm.

D. Management of Data

DC was calculated for each post-irradiation spectra using the uncured and cured peak ratios. At each post-irradiation sampling time, the average DC for the three samples of Filtek and the standard deviations calculated. The plotted data were used to characterize the time-dependent conversion.

IV. RESULTS

Several Filtek LS samples were piloted: a total of 3 were selected for evaluation because sampling times were identical and data collection continued for at least 10 days, although the longest observation period was 14 days for one sample. Plots of post-irradiation DC over time are shown in Figure 5.

Figure 5: DC vs post-irradiation time for all samples.
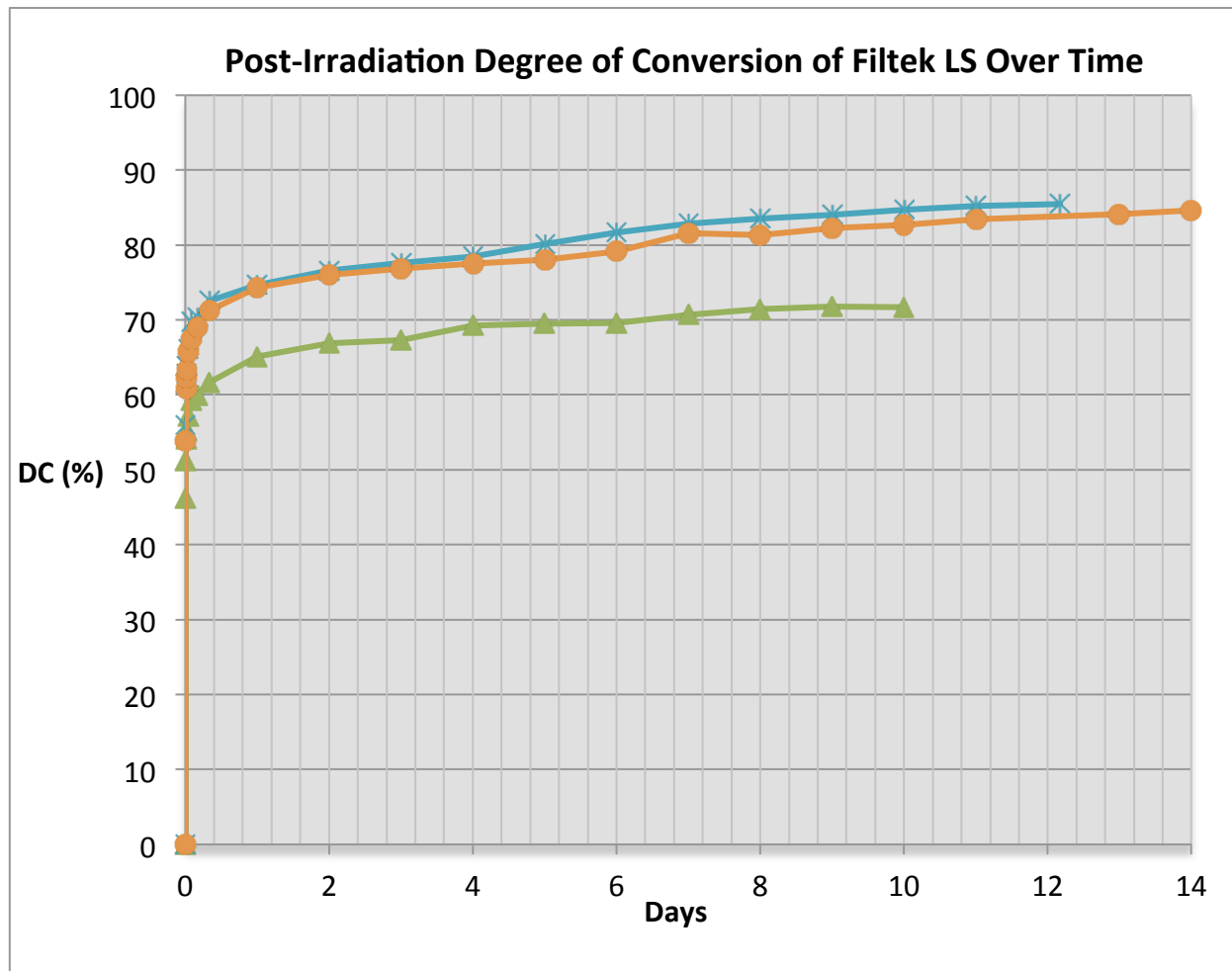
Observed values for immediate post-cure DC ranged from 39% to 58%. Values for DC at 10 days post-cure ranged from 72% to 85%. The highest measured DC for

any of the selected samples was 85.5% at 12 days. The latest post-irradiation time was at 14 days with a DC of 84.6%. Average DC and associated variance bars of the three selected samples were plotted over time over 10 days, the shortest time during which all 3 samples were observed (Figure 6). The average DC increased and seemed to plateau at 10 days at a DC of 80%. Standard deviation at each time point for the three samples ranged from 6.8 – 9.9%. If maximum conversion is assumed to occur on day 10, the data indicates 67% of total conversion occurs during photoinitiation, 80% after 1 hour, 88% in 24 hours, 90% in 2 days, 95% in 4 days, and 99% in 8 days. This represents an increase of DC from baseline of 53%, accounting for 35% of total conversion.

Figure 6: DC vs post-irradiation time for three samples (averaged) with standard deviation.
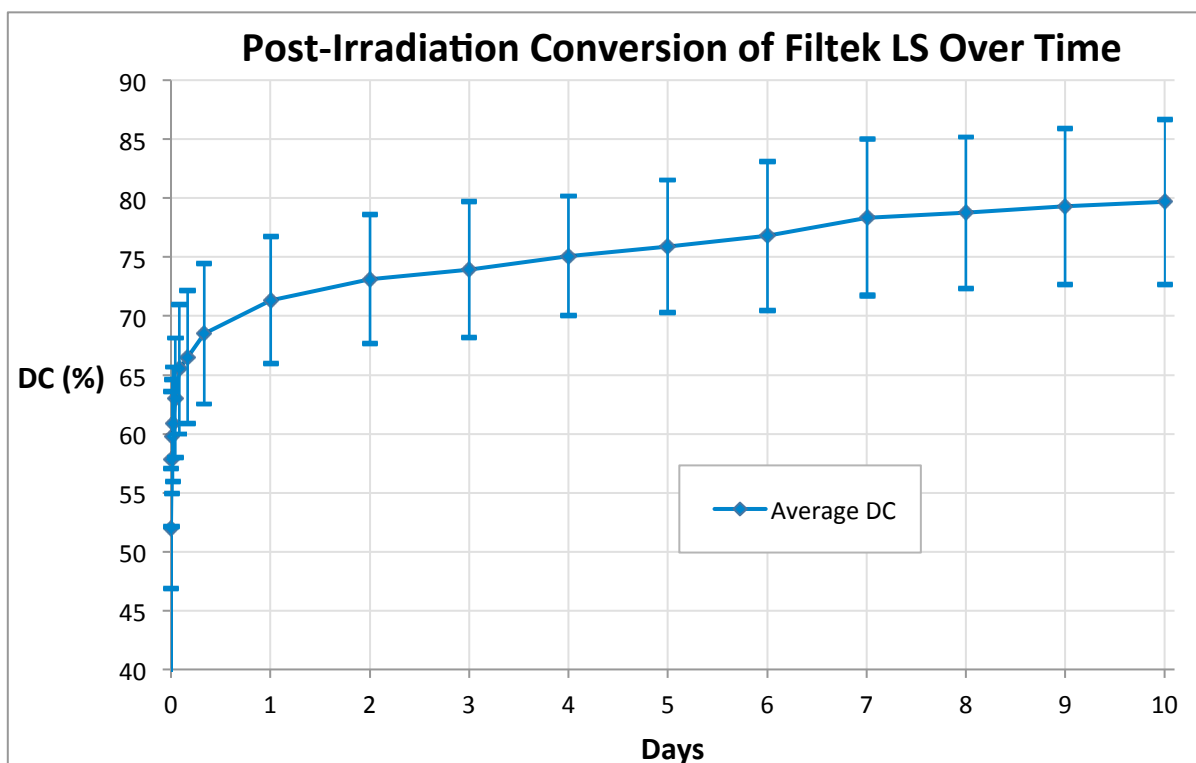
V.   DISCUSSION

A. Noise and Attachment of Sample to the ATR Element.

During initial piloting efforts, samples were made by inserting composite into molds, photoinitiating, and then placing the sample in contact with the ATR element. A torque of up to 100 N-cm was applied to maintain intimate contact between the ATR crystal and the sample. However, noise in the spectra made the variability so high that no trends could be detected in peak heights, or DC, over time.

It was theorized that air between the sample and the ATR crystal was the source of error. Therefore, samples were made by application of uncured composite to the ATR crystal and photoinitiating in place. Thereafter, spectra were obtained over the 10-day period without removing the sample from the ATR sample platform, with greatly reduced variability.

B. Degradation of Signal with Time for Some Samples

Numerous samples were discontinued before 10 days because of degradation of the signal. For some of the samples, this was due to software failure. For other samples, the degraded spectra seemed consistent with lack of intimate contact between sample and ATR element. Following degradation of the spectra, it was noted that no effort was required to remove the sample from the platform, supporting loss of

intimate contact or mechanical bond as the cause. Eventually by slightly increasing sample thickness and applying approximately 50 N-cm of torque to the uncured sample within the mold on the ATR sample platform, signals became more reliable. The technique used to apply torque to the uncured composite resulted in expression of some composite out of the mold onto the bordering, flat, area of mold (see Figure 1b). Despite the fact that the torque wrench was not in direct contact with the sample mold, which would be the only way to guarantee an exact and reproducible sample thickness, the expression of material did not affect the ability to reliably produce the desired sample thickness.

To compare the behavior of Filtek LS to methacrylates, the data was compared to the results presented by Leung (Leung et al, 1983). For both the top surfaces and the bottom surfaces of composites tested in that study, the extent of polymerization increased with post-exposure time. The general trend for a specific exposure time and surface was a slow increase in hardness values for the first 20 min after exposure, followed by gentle leveling off up to 60 min, and then slightly higher hardness values at one and seven days. In most cases, multiple comparison tests showed that there were no statistically significant differences for hardness values between 20 and 60 min of post-exposure, and between one and seven days. Thus, polymerization of the methacrylate composite continued at a slow rate after exposure and essentially reached a termination point at approximately one day.

Approximately 20% of total conversion was accounted for by post-irradiation polymerization at top surfaces.

In the present study, all samples demonstrated an initially rapid increase in DC, with the rate decreasing over time in a logarithmic-looking fashion visually similar to the data presented by Leung. Most post-irradiation conversion was completed within 24 hours; however, a continued slow rate of conversion accounted for an additional 10% DC increase over the next 9 days. As mentioned, this post-irradiation conversion accounted for 35% of total conversion. Therefore, the overall post-irradiation behavior of the silorane composite is similar to that of methacrylates in previous studies, but with a longer duration and higher amount of total conversion accounted for by post-irradiation polymerization. It is difficult to say whether the change in DC essentially stops after a certain point, or changes to a nearly linear, slow, increase that does not clearly stop completely after 10 days. This may be due to either continued polymerization or chemical degradation of reactive groups, causing loss of the reactive peak in the silorane spectra. Bouschlicher (1994) concluded that hardness was a more sensitive measure of conversion than DC. It is possible that post-irradiation hardness measurements would be a better indicator of continued polymerization over time after photoinitiation.

Final DC observed in this study was 80%. In previous studies, the DC of methacrylates has been measured at 44-74% (Chung and Greener, 1990). Since the present study measured DC of a thin sample simulating a top surface, DC is expected to be higher than at bottom surfaces of thicker samples, and the observed DC is comparable to that observed for methacrylates.

The samples were stored on the ATR element at room temperature and humidity. It is possible that post-irradiation polymerization would be different if the sample were at physiologic temperature and humidity.

The prolonged post-irradiation conversion observed in this study is consistent with previous findings (Palin et al, 2005). An experimental silorane was shown to have a slower post-irradiation conversion than methacrylate composites. Post-irradiation conversion continued over a period of 48 hours for siloranes whereas methacrylates had no signficant increases after 1 hour (Palin et al, 2003). The post-irradiation conversion was thought to explain increased cross-linking and tensile strength of the silorane. The delayed conversion was thought to be related to the cationic polymerization reaction. However, immersion in water was associated with decreased DC and physical properties. It was proposed that absorption of water molecules may compete with non-polymerized oxirane groups and cause premature termination of the polymerization reaction. (Palin et al, 2003).

stress of oxirane resin formulations reported in the literature has been attributed to the "living" or "dark" polymerization associated with the cationic mechanism (Tilbrook, et. al., 2000; Millich et. al., 1998; Palin, 2005). The cationic reaction has been previously referred to as a 'living' polymerization in that the reactive species of polymerizing oxiranes did not become extinguished as rapidly as the free radicals in methacrylate polymerization. This results in decreased polymerization kinetics of the oxirane compared with the methacrylate monomers and generates a temporary excess of free volume that enhances the mobility of polymer chains within the system. As a result, the polymerization efficiency of the cationic ring-opening monomers compared with the free radical species was increased and slowed development of flexural strength. The 'living' nature of the cationic polymerization may be manifested as an increased stress relaxation of the polymerizing silorane composite (Palin, et. al., 2005).

IV. CONCLUSIONS

The post-irradiation conversion of a silorane composite, Filtek LS, follows a pattern and rate (curve shape) similar to methacrylate composites. The proportion of conversion as measured by DC accounted for by post-irradiation conversion is slightly higher than that reported for methacrylates (as measured by hardness), and the duration of post-irradiation conversion is longer. Final degree of conversion is similar to that reported for methacrylates.

VII. DISCLOSURES

VIII. APPENDIX A- RAW DATA

Average DC and Standard Deviation for Filtek Samples 5, 6, and 7				
Time	Average DC	Ave +SDEV	Ave - SDEV	SDEV	SDEV%
0 min	51.96	57.06	46.86	5.10	9.81%
10 min	57.86	63.58	52.13	5.73	9.90%
20 min	59.76	64.61	54.91	4.85	8.12%
30 min	60.84	65.69	55.98	4.85	7.98%
1 hour	63.02	68.10	57.94	5.08	8.06%
2 hours	65.49	71.01	59.98	5.51	8.42%
4 hour	66.49	72.15	60.83	5.66	8.52%
8 hours	68.49	74.46	62.51	5.98	8.72%
1 day	71.34	76.75	65.93	5.41	7.59%
2 days	73.15	78.61	67.68	5.46	7.47%
3 days	73.94	79.71	68.17	5.77	7.81%
4 days	75.10	80.18	70.03	5.08	6.76%
5 days	75.90	81.52	70.28	5.62	7.40%
6 days	76.80	83.14	70.46	6.34	8.25%
7 days	78.36	85.02	71.70	6.66	8.50%
8 days	78.77	85.19	72.35	6.42	8.15%
9 days	79.34	85.96	72.71	6.63	8.36%
10 days	79.69	86.71	72.68	7.02	8.80%

Post-Irradiation Degree of Conversion for EsthetX and Filtek LS Over Time													
Filtek LS 1		Filtek LS 2 (0.42mm)		Filtek LS 3 (0.9mm)		Filtek LS 4 (1.0mm)		Filtek LS 5 (0.5mm)		Filtek LS 6 (0.6mm)		Filtek LS 7	
Time (Days)	DC (%)	Time (Days)	DC (%)	Time (Days)	DC (%)	Time (Days)	DC (%)	Time (Days)	DC (%)	Time (Days)	DC (%)	Time (Days)	DC (%)
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.001	57.694	0.001	51.046	0.001	39.125	0.001	52.183	0.001	46.195	0.001	55.872	0.001	53.827
0.008	65.760	0.007	58.788	0.008	46.015	0.009	58.736	0.007	51.251	0.008	61.443	0.009	60.873
0.016	65.864	0.014	62.194	0.015	47.866	0.015	60.137	0.014	54.166	0.015	62.825	0.016	62.281
0.023	67.284	0.021	62.890	0.022	48.454	0.022	62.028	0.021	55.240	0.022	63.895	0.023	63.372
0.044	66.991	0.042	65.114	0.043	50.875	0.043	63.633	0.042	57.158	0.043	66.120	0.044	65.791
0.088	70.877	0.083	66.729	0.085	51.809	0.085	66.016	0.083	59.275	0.085	69.773	0.088	67.437
0.298	74.104	0.319	70.500	0.168	54.237	0.169	68.838	0.168	59.992	0.169	70.376	0.170	69.096
1.308	77.956	0.998	74.059	0.335	55.167	0.334	69.556	0.333	61.629	0.336	72.559	0.336	71.278
2.305	78.607	1.324	75.394	1.003	58.168	0.999	71.795	1.001	65.094	1.001	74.647	1.002	74.275
3.293	81.931	1.994	76.959	1.335	58.950	2.000	73.886	2.001	66.847	2.003	76.554	2.002	76.036
5.303	86.190	2.331	78.031	2.003	60.790	3.002	74.939	3.001	67.287	3.005	77.636	3.001	76.890
6.003	84.391	2.333	78.219	2.335	61.260	4.001	75.358	4.000	69.268	4.004	78.494	4.011	77.547
6.006	84.343	2.989	79.981	3.002	62.558	4.999	75.868	4.999	69.524	5.002	80.118	5.003	78.058
6.010	84.964	3.000	79.974	3.343	62.701	5.999	76.805	6.005	69.624	6.004	81.641	6.002	79.132
6.014	84.867	3.331	80.999	4.003	62.512			7.001	70.708	7.003	82.834	7.002	81.546
6.036	84.361	3.996	82.179	4.337	64.006			8.001	71.465	8.003	83.511	8.002	81.340
7.015	85.231	4.334	82.421	5.001	62.959			9.001	71.749	9.005	84.008	9.002	82.249
7.988	86.237	4.996	83.564	5.347	63.605			10.002	71.675	10.003	84.711	10.002	82.692
		5.332	82.506	6.003	63.247					11.005	85.227	11.014	83.432
		6.017	84.408	6.339	63.331					12.177	85.483	12.989	84.105
		6.363	84.659	7.006	64.379							13.995	84.634
		6.999	85.320	7.335	63.834								
		7.328	85.737	8.003	64.006								
				8.335	64.090								
				9.001	64.469								
				9.335	64.455								

Filtek LS, all samples, DC over time.
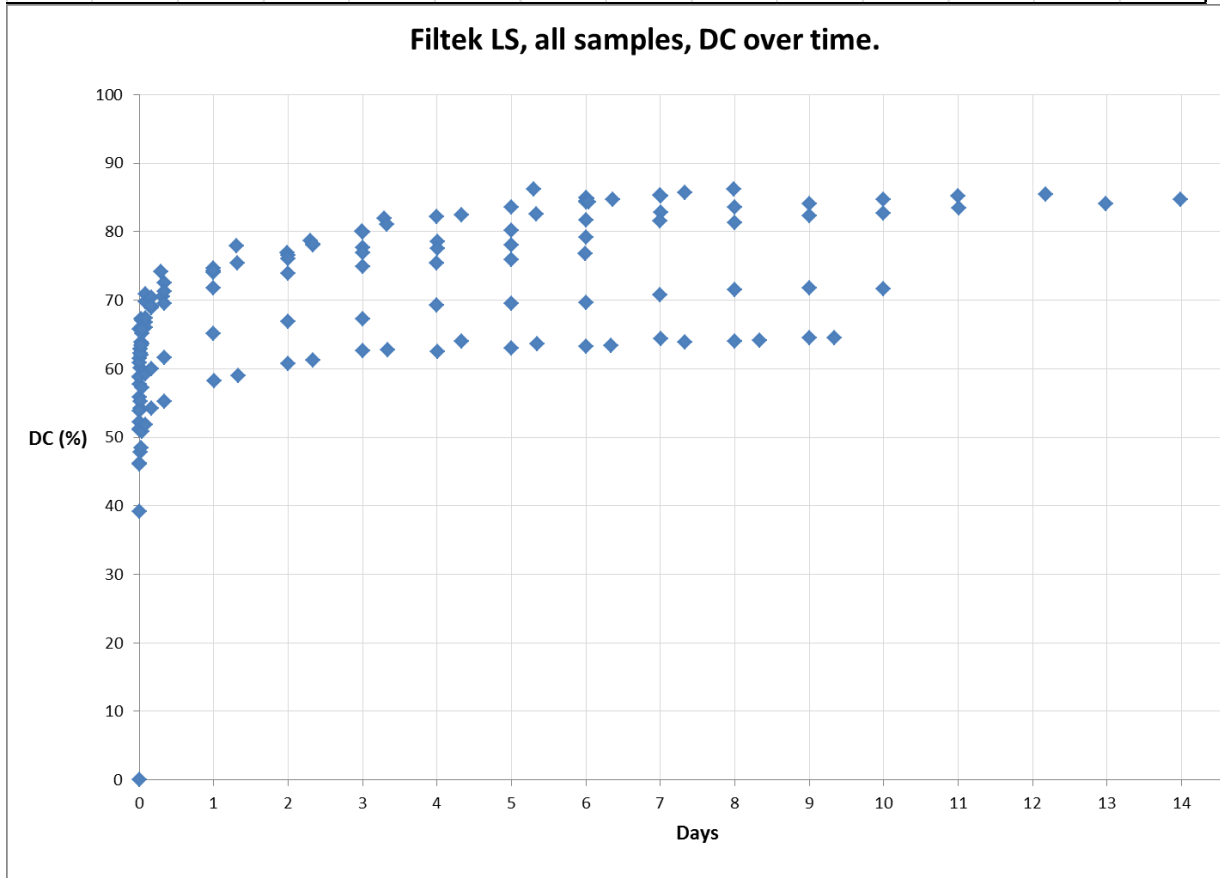
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